



## Analytical Methods

## Electrochemical determination of copper ions in spirit drinks using carbon paste electrode modified with biochar



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## ABSTRACT

This work describes for first time the use of biochar as electrode modifier in combination with differential pulse adsorptive stripping voltammetric (DPAdSV) techniques for preconcentration and determination of copper (II) ions in spirit drinks samples (Cachaça, Vodka, Gin and Tequila). Using the best set of the experimental conditions a linear response for copper ions in the concentration range of  $1.5 \times 10^{-6}$  to  $3.1 \times 10^{-5} \text{ mol L}^{-1}$  with a Limit of Detection (LOD) of  $4.0 \times 10^{-7} \text{ mol L}^{-1}$ . The repeatability of the proposed sensor using the same electrode surface was measured as 3.6% and 6.6% using different electrodes. The effect of foreign species on the voltammetric response was also evaluated. Determination of copper ions content in different samples of spirit drinks samples was also realized adopting inductively coupled plasma optical emission spectroscopy (ICP-OES) and the results achieved are in agreement at a 95% of confidence level.

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## 1. Introduction

Production and consumption of alcoholic beverages have been growing and promoting a large influence in several sectors like economic, social and health (Jernigan, Monteiro, Room, & Saxena, 2000; Room, Babor, & Rehm, 2005; Sierksma, Hulshof, Grobbee, & Hendriks, 2003). In general, several elements could be found in distilled beverages such as As, Pb, Zn, Fe and principally Cu (Cassella, Caldas, Francisco, & Pereira Netto, 2011; Nascimento-Filho, Cunha e Silva, Almeida, & Valencia, 2004). Despite of copper is an essential micronutrient required for numerous cellular functions (Double et al., 2013), the ingestion in excess of this metal, is toxic and may cause serious damages to health (Brewer, 2008; Nobrega, Neves, Oliveira, & Fernandes, 2007; Tapiero, Townsend, & Tew, 2003). Cachaça a distilled drink prepared from the fermentation of sugar cane, is one of the most popular alcoholic beverages consumed in Brazil (Pereira et al., 2012; Vicente et al., 2006). Brazilian legislation requires that copper concentration in the Cachaça should not be higher than  $5.0 \text{ mg L}^{-1}$  (Araujo, Almeida, Martins, Silva, & Moreira, 2003; Nascimento-Filho et al., 2004). The presence of large amounts of copper in Cachaça and other spirit drink can be attributed to the lixiviation from the distillation apparatus

during the production process of these drinks (Navarro et al., 2007). Thus, it is very important the development of analytical methods cheap, fast and reliable for the copper determination in alcoholic beverages.

The recommended method for determination of copper in distilled beverages in Brazil is the atomic absorption spectrometry using the method of standard addition (Zenebon, Pascuet, & Tinglea, 2008, chap. 9). There are other methods that can also determinate copper in beverages such as X-ray fluorescence spectrometry (Galani-Nikolakaki, Kallithrakas-Kontos, & Katsanos, 2002), atomic absorption spectrometry (Bermejo-Barrera, Jurado, Martín, Pablos, & Moreda-Piñeiro, 2007) and ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) (Bingöl, Yentür, Erand, & Öktem, 2010). However, these techniques are relatively expensive and, in most cases, require a complex and rigorous pre treatment of the sample to be analysed (Araujo et al., 2003; Nascimento-Filho et al., 2004). In this way, electroanalytical techniques have been widely evaluated as alternatives strategies to develop simple and precise methods for copper determination. From electroanalytical view, for determination of several metallic species is very common the use of stripping voltammetry (SV) combined with chemically modified electrodes (CME). The use of CME under SV conditions promotes not only an improvement of the detection limits but also a high sensibility allowing to reach greater selectivity for the analyte and sometimes eliminate the

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pretreatment of the sample (Ganjali, Motakef-Kazami, Faridbod, Khoei, & Norouzi, 2010; Janegitz, Marcolino-Junior, Campana-Filho, Faria, & Fatibello-Filho, 2009; Oliveira, Tanaka, Stradiotto, & Bergamini, 2012). The most important aspect is the choice of modifier which confers special characteristic to the electrode surface.

Biochar is a kind of carbonaceous obtained from thermal degradation of organic materials in the absence of air (pyrolysis) (Lehmann & Joseph, 2009, chap. 1–2). Several biomass such as agricultural crop residues, forestry residues, wood waste, and animal manures have been proposed as feedstock for biochar production. This product has a surface highly rich in functional groups, and these organic carbon components of biochar can stabilize heavy metals by (1) electrostatic interactions; (2) ionic exchange; (3) sorptive interaction; and/or (4) specific binding of metal ions by surface ligands (e.g., carboxyl, hydroxyl, phenol) abundant in the volatile matter component of biochar (Uchimiya, Bannon, Wartelle, Lima, & Klasson, 2012). Given the great efficiency of preconcentration of species, the biochar has been largely applied for the remediation of soils and waters contaminated by several species (organic and/or inorganic) (Uchimiya, Lima, Klasson, & Wartelle, 2010). In spite of significant adsorbent properties of the biochar its use in electroanalytical procedures is still poorly explored. Suguihiro et al. (2013) proposed recently the use of biochar as electrode modifier for Lead and Cadmium preconcentration applied with successful for waste water analysis.

Based on this, the present paper describes for first time a procedure for selective preconcentration and determination of copper ions in Cachaça and other spirit drink samples by applying anodic stripping analysis using the electrochemical characteristics of a carbon paste electrode modified with biochar. The method is based on the effective preconcentration of copper ions on the electrode surface containing biochar in open circuit conditions followed by the analyte reduction and subsequent anodic sweep under differential pulse voltammetry conditions.

## 2. Experimental

### 2.1. Apparatus

Differential pulse adsorptive stripping voltammograms (DPAdSV) were performed in a potentiostat/galvanostat  $\mu$ AUTO-LAB Type III (EcoChemie, Utrecht, Netherlands) connected to a microcomputer controlled by software (GPES 4.9, EcoChemie, Utrecht, Netherlands) for data acquisition and experimental control. All the voltammetric measurements were carried out in a 20 mL glass cell at 25 °C, with a three-electrode configuration: modified carbon paste electrode as the working electrode, Ag/AgCl KCl 3 mol L<sup>-1</sup> as the reference electrode and platinum plate as auxiliary electrode. During the measurements, the solution in the cell was not stirred. The pH measurements were carried out using a pH meter (Metrohm, Utrecht, Netherlands) with a combined pH reference electrode.

Preparation of biochars was realized from castor oil cake using an EDG FT-40 microprocessor-controlled furnace. The elemental composition (C, H and N) was determined using a Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer, Waltham, MA, USA). Information about functional groups present at surface of the biochar was provided by a FTIR Bomem MB100 spectrometer (Bomem Corp., Quebec, Canada) recording the spectrum scope from 4000 to 350 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

### 2.2. Reagents and solutions

All the solutions were prepared with purified water in a Milli-Q system (Millipore (Merck), Darmstadt, Germany). All the chemicals were of analytical grade and were used without further

purification. A stock solution containing 1000 mg L<sup>-1</sup> of copper ions (Merck, Darmstadt, Germany) was used. Ammonium and Acetate buffer solutions 0.1 mol L<sup>-1</sup> in different pH values were used as preconcentration solution and supporting electrolyte, respectively in all experiments. Different solutions of copper (II) ions were prepared by dilution of stock solution.

### 2.3. Experimental procedures

#### 2.3.1. Sensor construction

Biochar samples were prepared from castor oil cake, gridding in ball mills to a particle size of 80 meshes, it was placed in porcelain boats in the inner glass tube furnace microprocessor-controlled (EDG, São Carlos, São Paulo, Brazil). The factors used were: heating rate (10 °C min<sup>-1</sup>), final temperature (300 °C) and warm-up period (60 min).

Carbon paste (1.0 g) electrode was prepared by carefully mixing the graphite powder (45–75% (w/w)) (Sigma–Aldrich, St. Louis, MO, USA), with biochar sample at a varying ratio (0–30% (w/w)) and subsequently added to 0.250 g of mineral oil (25% (w/w)). The components were mixed manually in a mortar and pestle for at least 10 min to obtain an appropriate homogenization. Composite obtained was packed into an adequate support of electrode consisting of a plastic cylindrical tube (o.d. 5 mm, i.d. 3 mm) with a copper rod inside used as an external electric contact. Appropriate packing was achieved by pressing the electrode surface against a filter paper.

#### 2.3.2. Voltammetric procedures

Best analytical performance was found adopting a procedure with four steps: (1) copper ions had been directly preconcentrated at electrode surface in open circuit potential under controlled stirring in ammonium buffer solution at pH = 9.0; (2) After that, electrode was removed from the preconcentration cell, briefly rinsed with deionized water and placed in the electrochemical cell containing 10 mL of 0.1 mol L<sup>-1</sup> acetate buffer solution (pH 5.0); the reduction of the adsorbed ions was realized at controlled potential conditions; (3) Measurements of DPAdSV were registered and (4) Finally, the electrode surface was cleaned by putting it in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution.

#### 2.3.3. Interfering studies

For interfering studies a well-known amount of copper ions were spiked to an aliquot of 100.0 mL of simulated sample in order to reach maximum amount allowed by Brazilian Department of Agriculture (5 mg L<sup>-1</sup>). By a similar way, samples were prepared with potential interfering species using concentration according to Brazilian legislation (Ministry of Agriculture, Normative Instruction 13, June 29, 2005): Iron (2.0 mg L<sup>-1</sup>), Zinc (3.0 mg L<sup>-1</sup>), Arsenium (100 µg L<sup>-1</sup>), Lead (200 µg L<sup>-1</sup>). The pH was adjusted at 9.0 and preconcentration step was realized directly by immersion of the CPME in the solution. Effect of the interfering ions was verified by comparing the anodic current of copper ions in presence and absence of the foreign species.

#### 2.3.4. Sample preparation and copper determination

Determination of copper ions was realized by analysis of several spirit drink samples (commercial Cachaça, homemade Cachaça, Vodka, Gin and Tequila) adopting both stripping voltammetric method and inductively coupled plasma optical emission spectroscopy (ICP-OES) using triplicate of each sample available. Samples have purchased from local stores and the trademarks were chosen because are relatively common in Brazil. For comparison reasons, all samples examined had been produced recently, stored in the dark and analysed shortly after opened. Aliquots of original samples were evaporated until certain of the initial volume and after

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